

PATENT SPECIFICATION (11)

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(54) TITANIUM DIOXIDE PIGMENTS

- (71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to titanium dioxide. More particularly, this invention relates to a process for the production of substantially non-greying, titanium dioxide pigments for use in resin compositions by after-treatment with basic aluminium nitrate or basic aluminium chloride solutions in the presence of colourless, oxygen-containing salts having an oxidising effect.
- Resin compositions, especially melamine-formaldehyde, urea-formaldehyde and phenol-formaldehyde resins are widely used on an industrial scale. Laminates, i.e. pressed multilayer materials in which the resin holds together individual layers of, for example, wood, paper, polymers or glass fibres, providing them with strength and hardness have a particularly wide range of application. Laminates in this form can be processed into scratch-resistant table coverings, boards or furniture and panelling for example. Since some of the aforementioned resin compositions are soluble in water, they can be opacified relatively easily by incorporating different pigments. It is possible in this way significantly to broaden their range of applications.
- One pigment that is particularly suitable for this purpose is titanium dioxide. However, it has been known for some time that titanium dioxide is photochemically active. In phenol-, melamine- or urea/formaldehyde-based laminates pigmented with TiO_2 , exposure to UV-light results in steadily increasing greying which can be attributed to a blue-grey discolouration of the TiO_2 -pigment incorporated. Attempts have been made over a long period to reduce the photo-activity of rutile pigments by subjecting them to an aftertreatment. However, effective reduction can only be achieved by subjecting the aftertreated pigments to an expensive and complicated calcination treatment. Attempts have also been made to produce pigments with adequate photostability in laminates by special aftertreatment which eliminate the need for subsequent calcination.
- The aftertreatment of titanium dioxide pigments with a few basic transition-metal salts, for example titanil sulphate (United States Patent Specification No. 2,214,132 and British Patent Specification No. 252,262) and also with special basic aluminium salts (United States Patent Specification No. 2,357,101) can be regarded as pertinent prior art. German Offenlegungsschrift No. 2,046,739 and British Patent Specification No. 1,134,249 describe an aftertreatment process using specially prepared aluminium salt solutions which are based on stoichiometrically composed aluminium salts, for example aluminium trichloride or aluminium nitrate, and, in one case by the addition of alkali, increase the pH-value without formation of a deposit, the quantity of alkali being adjusted so that it amounts to between 25 and 70 mol% of that quantity of alkali which would be necessary for completely replacing all the anions of the salt used. The solution which, in addition to the partially neutralised aluminium salt, also contains the alkali salts formed, is then subjected to an ageing process in the course of which it is heated to a temperature of from 40 to 90°C for from 30 to 60 minutes. This aged solu-

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tion is then used for the usual aftertreatment, giving pigments with particularly dense aluminium oxide layers and improved service properties. Unfortunately, rutile pigments aftertreated by the aforementioned processes do not show the photostability of after-treated pigments that have been subjected to calcination in the aforementioned resin systems.

10 United States Patent Specification No. 3,427,278 describes resin systems which contain titanium dioxide pigments and which are photochemically inert. From 0.1 to 5% of nitrate is incorporated in these resin systems. The disadvantage of this process is that the nitrates added are soluble in water and, in the case of hydrolytic dissociation, have a polymerising effect upon the resins and complicate processing by hardening the resin.

20 We have sought to prepare pigments which can readily be incorporated with adequate photostability into resin-based laminates without any need for complicated and expensive aftertreatment by calcination.

25 Accordingly, the present invention provides a process for the production of a substantially non-greying, titanium dioxide pigment coated with a layer of aluminium oxide aquate which comprises:

30 (a) either (i) adding a solution of a basic (as hereinafter defined) aluminium nitrate and/or a basic aluminium chloride, and a colourless oxygen-containing salt having an oxidising effect, to an aqueous suspension of a titanium dioxide pigment; or (ii) suspending a titanium dioxide pigment in the basic aluminium nitrate and/or basic aluminium chloride solution before adding the oxygen-containing salt;

35 (b) adding to the resulting suspension in (a) (i) or (a) (ii), followed by adding the oxygen containing salt in the case of the suspension from (a) (ii), an alkali in order to precipitate aluminium oxide aquate containing the anion of the colourless, oxygen-containing salt; and

40 (c) separating the resulting titanium dioxide pigment coated with a layer of the aluminium oxide aquate from the aqueous medium and drying the pigment.

45 The process according to the invention is based on the concept of using for the aftertreatment basic aluminium nitrate and/or chloride salts in which there is a deficit of anions (disregarding the OH-anion) in relation to the aluminium cations. The word "basic" is not intended to imply an alkaline reaction of these salts, but only to express the fact that, in purely stoichiometric terms, these salts contain OH-anions. Compounds having a ratio of aluminium cation

to nitrate or chloride anion of from 0.5 to 5, preferably from 1.0 to 3.0 (disregarding OH as anion), are suitable for the purposes of the invention. Examples of compounds such as these include

Al(OH)₃(NO₃)_{0.5} (cation: anion ratio 2),
Al(OH)₃NO₃ (cation: anion ratio 1),
Al(OH)₂(NO₃)₂ (cation: anion ratio 5),
Al₂(OH)₅Cl (cation: anion ratio 2).

Basic salts of this kind can be prepared by any one of the known methods for producing basic aluminium salt solutions (cf. Gmelins Handbuch der Anorg. Chemie, 8th Edition, No. 35, Al part B, pages 117-125, 156 *et seq.*, 205 *et seq.* (1934), for example by dissolving aluminium metal in a deficit of nitric acid or hydrochloric acid or by peptising Al(OH)₃ in a deficit of acid. Coating the pigment particles with a layer of aluminium oxide aquate is carried out by slowly and steadily increasing the pH-value of an aqueous pigment suspension with the basic aluminium salt solution added to it, with alkali metal or ammonium hydroxide or alkali metal carbonate at a temperature in the range of from 10 to 40°C.

The basic aluminium salt solutions used in accordance with the invention contain particles of the colloidal order of magnitude. It is possible to speak in terms of an aluminium oxide sol which is impoverished in anions (disregarding OH as an anion). The preparations of sols such as these is not dependent upon a special ageing process. By increasing the pH-value of the solution, the aluminium oxide sol is converted into an aluminium oxide gel which forms the layer of aluminium oxide aquate on the pigment particles. Since the aluminium oxide sols according to the invention are more impoverished in anions than sols of the kind obtained by neutralising aluminium salts, anions additionally added to the system can readily be incorporated into the oxide gel formed by conversion of the oxide sol during the conversion process. According to this invention, the anions of colourless oxygen-containing salts having an oxidising effect, preferably nitrates, nitrites, peroxy sulphates and H₂O₅⁻ or peroxide-addition compounds, for example perborates such as BO₂ · H₂O₅⁻ are incorporated into the aluminium oxide aquate layer formed. Mixtures of these salts containing anions having an oxidising effect can also be used for the after-treatment. To this end, solutions of salts containing these anions are added to the suspended pigment suspension before or during conversion of the oxide sol into oxide gel by increasing the pH. In one advantageous embodiment, the process according to the invention comprises the following stages:

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- (1) Preparing the basic aluminium salt solution.
 - (2) Making the pigment into a suspension with the basic aluminium salt solution.
 - (3) Increasing the pH of the pigment suspension as uniformly as possible by addition of alkali (spraying in or on, pumping) to a pH value of from 5.0 to 6.0 over a period of from 0.25 to 2 hours.
 - (4) Adding an aqueous solution of an oxidising salt at a pH value of the aluminium-salt-containing pigment suspension of from 5.0 to 6.0.
 - (5) Increasing the pH value of the pigment suspension as homogeneously as possible to a value of from 6.0 to 7.0 over a period of from 0.5 to 4 hours.
 - (6) Increasing the pH value of the pigment suspension as homogeneously as possible to a value of from 7.0 to 8.0 over a period of from 15 to 60 minutes.
 - (7) Washing with cold water, drying and grinding the aftertreated pigment.
- The drying mentioned as item 7 can be carried out at a relatively low temperature in the range of from 25°C to 250°C, in practice at a temperature of from 120°C to 200°C. The purified filter sludge can be dried in any way, for example in a drying cabinet, thin-layer evaporator, belt dryer, cylinder dryer or by spray drying. The relatively low drying temperatures are explained by the fact that there is no need during drying to remove any salts incorporated in the system.
- Following the aftertreatment, the titanium dioxide pigments produced by the process according to the invention contain from 0.5 to 10% by weight, and preferably from 2.0 to 5.0% by weight (based on TiO_2), of aluminium oxide in the form of a layer of aluminium oxide aquate. Anions having an oxidising effect are incorporated in this layer of aluminium oxide aquate so that the resulting pigment contains from 0.05 to 1.0% by weight (based on TiO_2), preferably from 0.2 to 0.6% by weight, of anions of the oxidising salts. Nitrate salts are preferably used only in quantities of from 0.05 to 0.4% by weight nitrate, based on the pigment.
- In order to modify the properties of the pigment, the aftertreatment process according to the invention can be followed or preceded by other aftertreatment stages known *per se* (for example additional precipitation of SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , SnO_2 , MgO , ZnO and phosphates or organic aftertreatment with amines, hydroxy alkanes, epoxides).
- Any TiO_2 -pigments produced either by the chloride process or by the sulphate process can be used for the process accord-

ing the the invention. Particularly suitable pigments are TiO_2 -pigments of rutile structure which already have an aluminium-oxide-modified surface, i.e. TiO_2 -pigments which have been produced for example by the combustion of TiCl_4 in the presence of AlCl_3 or by the calcination of a TiO_2 hydrolysis sludge in the presence of Al_2O_3 , although the invention is by no means limited to these types of pigment.

By comparison with TiO_2 -pigments aftertreated with SiO_2 and Al_2O_3 and then calcined, the TiO_2 -pigments aftertreated in accordance with the present invention are lighter, show a more pronounced blue tint and, in some cases, considerably greater brightening power. They show outstanding resistance to greying in laminates. Melamine/formaldehyde-, urea/formaldehyde- or phenol/formaldehyde-based laminates can contain the TiO_2 -pigments aftertreated in accordance with the invention advantageously in quantities of from 1.0 to 40% by weight (based on the laminate).

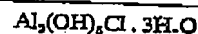
In order to test laminate stability, laminates were prepared with different TiO_2 -rutile pigments. More particularly, the following procedure was adopted:

100 g of a melamine-formaldehyde resin were made into a paste with 60 ml of distilled water at 60 to 70°C using a glass rod, some of ethanol were added and the resulting paste was stirred with a glass stirrer until the melamine resin was completely dissolved. The solution obtained kept for only 1 day.

12.5 g of ground TiO_2 -pigment are weighed into a glass beaker, 100 g of the above resin solution added and the components stirred for 5 minutes with an intense stirrer, 7500—8000 r.p.m. working on stator-rotor principle.

After the dispersion had been transferred to a porcelain dish, four strips of filter paper (Whatman No. 3) were semi-immersed one after the other, the saturated half fixed in a paper clip and then the other half immersed. In order to prevent the dispersion from dripping off, both sides of the paper were stripped with a glass rod over the dish. The paper clips with the impregnated strips hanging from them were suspended from a wire frame and left to dry for 20 minutes at 100°C. After cooling, the paper strips were drawn through unpigmented resin solution and stripped as just described. The specimens were then tempered for 20 minutes in a drying cabinet preheated to 138°C. The four strips of each specimen are placed one on top of the other, written on and placed between two clean, chromium-plated steel plates. The specimens were pressed for 13 minutes under a pressure of 105 kg/cm² in a hydraulic two-column laboratory hand press with heating and cooling means which has been preheated to 149°C. Thereafter, the

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heating was switched off with the pressure intact and, for cooling to 40°C, the water cooling system was brought into operation for 3 to 4 minutes. After a temperature of 40°C had been reached, the press could be opened and the pair of plates with the specimen in between removed.

The pigmented laminate panels were tested for brightness before exposure and for percentage greying after exposure.

To this end, the reflectance of the panels was determined from the lower half of the panel by means of an electrical remission photometer using a standardised green filter (Ry filter). The reflectance value Ry determined is a measure of the brightness. The upper half of the plates was then masked with an aluminium foil in order subsequently to see the contrast between the exposed and unexposed surface. The masked side was placed on the edge of a rotating disc (3 r.p.m.) and, after the specimens had been exposed for 4 hours to the light of 6 Ultra-Vitalux (Registered Trade Mark) lamps (arranged in a circle at a distance of 10 cm from the rotating disc), the Ry-value was measured at the same place on the specimen as before exposure. The expression

(Ry before—Ry after exposure) . 100

Ry before exposure

indicates the percentage greying.

In addition to brightness and percentage greying of the laminate panels, the brightening power of the pigment powder was measured in accordance with DIN 53 192; its blue tint was also measured. The difference between the reflectance of blue and red filter ($R_b - R_r$) on a grey paste rubbing with $R_y = (35 \pm 0.2)\%$ served as a measure of the blue tint. This difference is known as the grey value. A more strongly positive grey value is indicative of a more pronounced blue tint and greater fineness of the pigment particles.

Brightening powder and grey value were determined after the pigment has been ground for 60 minutes in a pulveriser. The described pigments were worked into laminates after grinding for 15 minutes in this mill.

The invention is illustrated by the following Examples:

EXAMPLE 1

125 g of a TiO_2 pigment which had been prepared by the sulphate process, calcined in the presence of Al_2O_3 (0.7% by weight, based on TiO_2) and then ground in a Raymond mill, were made into an aqueous suspension at room temperature with 950 ml of water and 1 ml of 10% HCl by means of a dissolver. A solution of 7 g of

was added to this suspension which had a pH-value of around 7, reducing its pH-value to 4.65. The pH-value of this suspension was then adjusted to 5.4 over a period of 2.25 hours with 92 ml of a 0.1 normal soda lye, and to 6.0 over another 2.5 hours with another 83 ml of the 0.1 normal soda lye. The 83 ml of the 0.1 normal soda lye used additionally contained 2.26 g of ammonium peroxy disulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Thereafter, the pH-value of the weakly acid solution was adjusted to 7.5 with another 113 ml of 0.1 normal soda lye which, on this occasion, did not have any ammonium peroxy disulphate added to it. The pigment suspension was then filtered, washed with 2 litres of neutral, desalted water and dried for 4 hours at 180°C. The resulting pigment was then worked into a paper laminate and subjected to the laminate test. The percentage greying measured amounted to 1.3%. The pigment contained 3.1% by weight of Al_2O_3 and 0.27% by weight of $\text{S}_2\text{O}_8^{2-}$ (based on the weight of the pigment). The brightening power according to DIN 53 192 amounted to 670, whilst the grey value measured 3.5.

EXAMPLE 2

563 g of the pigment described in Example 1 were made into a suspension with 1150 g of H_2O and 168 ml of a basic aluminium nitrate solution of the composition



The basic aluminium nitrate solution had been prepared by dissolving coarse aluminium powder in a deficit of HNO_3 , and contained 85 g of Al_2O_3 per litre. The pigment suspension had a pH-value of 4.15. The aqueous pigment suspension was then adjusted to a pH-value of 5.5 with 18 ml of 5% NaOH added over a period of 1 hour. In the interests of thorough distribution, the soda lye was introduced into a glass rotary pump by which the suspension was pumped around. An aqueous solution of 3.76 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 225 ml of water was then introduced dropwise into the pigment suspension over a period of 30 minutes, after which the pH-value fell to 5.35. By introducing more 5% NaOH, the pH-value was adjusted to 6.6 over a period of 2 hours and to 7.5 over a period of another 30 minutes (60 ml of 5% NaOH). The pigment suspension was filtered, washed with 5 litres of cold water and, finally, the filter cake was dried for 4 hours at 180°C. The pigment worked into a laminate (starting reflectance Y-filter 85%) showed a percentage greying of 1.2% after exposure to light. It contained 3.2% by weight of Al_2O_3 , 0.1% $\text{S}_2\text{O}_8^{2-}$ and 0.1% of NO_3^- (based on TiO_2). The brightening power according to DIN 53 192 amounted to 720 and the grey value to 3.6.

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EXAMPLE 3

625 g of the pigment described in Example 1 were made into a suspension with 4800 ml of H₂O and 195 ml of the basic aluminium nitrate solution described in Example 2 (A 2.5% by weight of Al₂O₃). The pH-value was adjusted to 5.0 by addition of 0.4% NaOH over a period of 30 minutes and then, in a second stage, the pH was increased to 7.5 by the uniform addition of 0.4% NaOH over a period of 6 hours during which the pigment suspension was adequately stirred. The second batch of soda lye contained 4.3 g of NaNO₂ in solution. The pigment worked up as in Example 2 and worked into the laminate showed a percentage greying of 1.0% after exposure to light. The pigment-optical data correspond to the details given in Example 2. The pigment contained 3.1% by weight of Al₂O₃ and 0.15% by weight of NO₂+NO₃, based on TiO₂.

Copending Applications Nos. 6222/73 (Serial No. 1,422,576), and 6782/73 (Serial No. 1,422,577) are both concerned with the manufacture of titanium dioxide pigments. Application No. 6782/73 (Serial No. 1,422,577) claims a titanium dioxide pigment coated with from 0.5 to 10% by weight of aluminium oxide aquate (calculated as Al₂O₃) and with 0.05 to 3.0% of nitrate, nitrite, peroxy disulphate or perborate (BO₂H₂O₂—) or a mixture of these anions.

Application No. 6222/73 (Serial No. 1,422,576) claims a process for the production of a substantially non-greying, titanium dioxide pigment coated with a layer of aluminium oxide aquate, wherein a solution of a basic aluminium nitrate is added to an aqueous titanium dioxide pigment suspension, or a titanium dioxide pigment is suspended in a solution of a basic aluminium nitrate and the resulting suspension is dried at a temperature in the range of from 25°C to 200°C.

Application No. 6222/73 (Serial No. 1,422,576) also claims a titanium dioxide pigment coated with from 0.5 to 10% by weight of aluminium oxide aquate (calculated as Al₂O₃) and with 0.05 to 3.0% by weight of nitrate anions when produced by the above claimed process.

WHAT WE CLAIM IS:—

1. A process for the production of a substantially non-greying, titanium dioxide pigment coated with a layer of aluminium oxide aquate which comprises:

(a) either (i) adding a solution of a basic aluminium nitrate and/or a basic (as hereinbefore defined) aluminium chloride, and a colourless oxygen-containing salt having an oxidising effect to an aqueous suspension of a titanium dioxide

pigment; or (ii) suspending a titanium dioxide pigment in the basic aluminium nitrate and/or basic aluminium chloride solution before adding the oxygen-containing salt;

(b) adding to the resulting suspension in (a) (i) or (a) (ii) an alkali, followed by adding the oxygen containing salt in the case of the suspension from (a) (ii), in order to precipitate aluminium oxide aquate containing the anion of the colourless, oxygen-containing salt; and
(c) separating the resulting titanium dioxide pigment coated with a layer of the aluminium oxide aquate from the aqueous medium and drying the pigment.

2. A process as claimed in claim 1, wherein the basic aluminium nitrate or chloride compound has a ratio of aluminium cation (Al³⁺) to nitrate anion or chloride anion of from 0.5 to 5.

3. A process as claimed in claim 2, wherein the basic aluminium nitrate or chloride compound has a ratio of aluminium cation (Al³⁺) to nitrate anion or chloride anion of from 1.0 to 3.0.

4. A process as claimed in any of claims 1 to 3, wherein a compound of the approximate stoichiometric composition $Al(OH)_{2.5}(NO_2)_{0.5}$ is used as the basic aluminium nitrate.

5. A process as claimed in any of claims 1 to 3, wherein a compound of the approximate stoichiometric composition $Al(OH)_{2.5}(NO_2)_{0.5}$ is used as the basic aluminium chloride.

6. A process as claimed in any of claims 1 to 5, wherein the resulting titanium dioxide pigment contains from 0.5 to 10% by weight of aluminium oxide aquate (calculated as Al₂O₃).

7. A process as claimed in claim 6, wherein the resulting titanium dioxide pigment contains from 2 to 5% by weight of aluminium oxide aquate (calculated as Al₂O₃).

8. A process as claimed in any of claims 1 to 7, wherein the layer of aluminium oxide aquate contains from 0.05 to 1% by weight based on TiO₂ of the anions of the oxygen-containing salt.

9. A process as claimed in claim 8, wherein the layer of aluminium oxide aquate contains from 0.2 to 0.6% by weight based on TiO₂ of the anions of the oxygen-containing salt.

10. A process for the production of titanium dioxide pigments coated with a layer of aluminium oxide aquate, wherein a basic aluminium nitrate and/or basic aluminium chloride solution is added to an aqueous titanium dioxide pigment suspension; the pH-value of the resulting pigment suspension is adjusted with alkali to a value of 130

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- from 5 to 6; an aqueous solution of oxygen-containing salt having an oxidising effect is added; the pH-value of the pigment suspension is adjusted to a value of from 6 to 7 in a first sequence and to a value of from 7 to 8 in a second sequence; and wherein the pigment suspension is washed with water and then dried.
11. A process as claimed in any of claims 1 to 10, wherein the alkali is added to the suspension at a temperature of from 10°C to 40°C.
12. A titanium dioxide pigment coated with from 0.5% to 10% by weight of aluminium oxide aquate (calculated as Al_2O_3) and with 0.05 to 1.0% by weight of peroxy disulphate, nitrite, nitrate or perborate ($BO_2H_2O_2$) anions or a mixture of these anions when produced by a process as claimed in any of claims 1 to 11.
13. A titanium dioxide pigment as claimed in claim 12, coated with from 2 to 5% by weight of aluminium oxide aquate (calculated as Al_2O_3).
14. A titanium dioxide pigment claimed in claim 12 or 13, in which the coating contains from 0.05 to 0.4% by weight of nitrate anions.
15. A titanium dioxide pigment as claimed in claim 13 substantially as herein described with reference to any of the specific Examples.
16. A process as claimed in claim 1, substantially as herein described with reference to any of the specific Examples.
17. A pigment when prepared by a process as claimed in any of claims 1 to 11 and 16.
18. Melamine/formaldehyde-, urea/formaldehyde- or phenol/formaldehyde-based laminates containing from 1.0% by weight to 40% by weight (based on the laminate) of a TiO_2 -pigment as claimed in any of claims 12 to 15 and 17.
19. Laminates as claimed in claim 18 substantially as herein described.

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